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F. A. Marion and H. J. McSpadden

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Representative: Bill, Dr. W; Hoeppener, A.; Wolff,

Dr. H. J.; Beil, Dr. H. C.;

Attornies at Law, 6230 Frankfurt-Hochst

Named as Inventor: Marion, Frank Allen; McSpadden, Hugh Joseph;

Riverside, California (U.S.A.)

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HEAT INSULATING MATERIAL AND PROCESS FOR ITS MANUFACTURE

F. A. Marion and H. J. McSpadden

The invention concerns a heat-insulating material able to resist high temperatures of several thousands of degrees C over a period of several hours, without being destroyed, and the process for its manufacture. /1*

For innumerable different applications it becomes more and more important to find a material that is able to withstand temperatures of several thousand degrees over a period of several hours. For instance, when rockets and space capsules travel both through or outside the atmosphere they are exposed to strong aerodynamical heat buildup and aerodynamical stress loads which cause the shell of the rockets and space capsules to assume over a short period of time temperatures of several thousand degrees. In another example, compressed gases blowing at high speeds through pipes and Venturi tubes create relatively high temperatures on the surface of such tubes and pipes. /2

Many experiments have been conducted in the past in order to find a material that would be able to withstand temperatures of several thousand degrees for long period of time, however such experiments have not been very successful. As an illustration, asbestos has been used as a heat insulating material. This material is, however, heated up to a temperature in the magnitude of 1,650°C, as is the case under the concentrated flame of an air acetylene burner, a layer of a wall thickness of 1.72 centimeters will allow the surface on the side opposite the air acetylene flame to reach in a few minutes the temperature of 316°C. Additionally, many heat insulating materials developed to date did not have the capability of being combined with different base materials, for instance metals, and were not in a position to preserve this bond if they were subject to high temperatures for a longer period of time. Many of the heat-insulating materials have also the tendency to crack and to lose their strength in a relatively short period of time.

*Numbers in the margin indicate foreign pagination.

The material claimed in the invention overcomes these disadvantages. For instance, the material was applied in a thickness of approximately 1.5 centimeters on a steel plate of a thickness of 0.12 centimeters and overall dimensions of approximately 15 × 15 centimeters. The flame of an air acetylene burner was directed upon the surface of the coating obtained so that a temperature of approximately 1,650°C and a heat transfer of approximately 162 'kcal/m² were achieved. After approximately one hour the steel plate temperature was only /3 approximately 93°C and after 30 hours only approximately 177°C. The material may be combined with any desired base material and it can also be applied in any desired thickness since it can be applied in liquid, plastic or solid form. The material may be handled and hardened at ambient temperatures between approximately 10 and 51.5°C. The material retains its properties even after it has been exposed for a long period of time to ambient temperatures and even if it has been in contact with solvents such as water, oil, benzene or toluene. The material retains its strength and/or its bond properties with the base material even if it has been exposed for long periods of time to intensive heat at several thousand degrees. The invented material may be used as an adhesive since it binds and spreads on other materials after hardening, filling cracks and pores.

The drawings show:

Figure 1. Cross-section showing the invented material applied on an insulated part.

Figure 2a. The temperature increase in the invented material.

Figure 2a. The temperature increase in the invented material. \

Figure 2b. The temperature increase with known materials.

Figures 3, 4 and 5. Show the temperature time relationship for the invented material and other known materials, when flames of relatively high temperature are continuously directed upon the materials for approximately 60 minutes and Figure 6 shows the temperature-time relationship of the invented material /4 when flames of relatively high temperature are directed uninterruptedly for approximately 50 hours upon the materials.

Figure 1 shows an invented application. It contains a steel plate 10, which is to be heat-insulated. The invented material is shown as a layer or coating 12 bound to the steel plate 10. The heat influence upon the insulated layer 12 is represented schematically by an acetylene burner 14.

The invented material consists of a binder and a filling material in the binder. The binder may be prepared as a mixture of a polysulfide and an epoxy in proportion of approximately 9:1 of the polysulfide weight. The preferred range is 70:30 weight parts of polysulfide to 30:70 weight parts of the epoxy. Typically the epoxy may be represented in a range from 45 to approximately 55 parts with the polysulfide making up the rest of the binder. The actual preferred proportion is approximately 50 weight parts of polysulfide and 50 weight parts of epoxy. The proportion depends upon the properties desired of the binder. For instance, the epoxy tends to be brittle and glassy, while showing high strength and small elongation. The polysulfide tends towards higher elasticity and lower tensile strength. Changes in the polysulfide and epoxy ratios influence the physical and structural property of the hardened binder matrix and the hardening speed.

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The filling material may be prepared from a mixture of phosphate and borate. The filling material consists preferably of a mixture of monobasic ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and anhydrous sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$). It should be also pointed out that the filling materials could also be monobasic sodium phosphate and anhydrous ammonium borate without particularly influencing the advantages of the resulting material. The monobasic ammonium phosphate may appear in a proportion of from 10 to 155 parts of the filling material while the anhydrous sodium borate may be present in quantities of 10 to 90 weight parts of the filling material. Preferably the amount of monobasic ammonium phosphate should be in the range of 35 to 80 parts of the filling material which also applies for the anhydrous sodium borate. Typically the anhydrous sodium borate may represent 55 weight parts and the monobasic ammonium phosphate 45 weight parts. The filling material may contain from 100 to 300 weight parts relative to 100 weight parts of the binder. Preferably the filling materials should represent approximately 150 weight parts while the binder corresponds to 100 weight parts.

The invented material may be prepared from two separate mixtures which may be stored separately, preferably in liquid form for as long as the raw material is being prepared. One of these mixtures consists of the polysulfide and a proportional amount of filling material which should be in form of a fine powder of a particle size of approximately 74 μ . A larger proportion of filling material than the proportion in the total mixture may be added to the polysulfide since the polysulfide is less viscous than the epoxy. The first mixture can be pre- /6
served for unlimited time at room temperature without losing its properties.

The first mixture contains a hardening material for the epoxy. The hardener is preferably a polyamine at a level of approximately 8 to 12% relative to the epoxy weight. The weight range of the polyamine may, however, be from approximately 0 up to 25% of the epoxy weight. Typically the polyamines are used at a level of approximately 10% by weight. It is, however, also possible to use polyamides and/or acid anhydrides. Polyamines and polyamides may be used together as hardeners but acid anhydrides must be used alone. If polyamides are used as hardeners their weight may be between 25 and 200% of the epoxy weight. A typical value would be 50% of epoxy weight.

The second mixture contains the epoxy and a proportional amount of filling material in the form of a fine powder of a particle size of approximately 74 μ . The second mixture is also kept in liquid form and may also be kept for an unlimited period of time at ambient temperature without losing its properties. When it is desired to prepare the invented material the first and the second mixture are mixed together at room temperature in the desired proportions and allowed to harden. After a certain period of time, for instance overnight, the material becomes relatively strong and possesses already approximately 70 to 90% of its consistency. The material may be used for most purposes even after this short period of time. Preferably, however, it should be allowed to harden for a /7
longer period of time, for instance, approximately a week before using.

The combined mixture of the first and second mixtures should be preferably hardened at room temperature, yet it may be hardened at temperatures up to 82 to 88°C. The combined mixture is preferably hardened at room temperature because this makes the formation of the material simpler. When the combination of the first and second mixtures are hardened at higher temperatures, the hardening

process is thereby accelerated. On the other hand, if an acid anhydride is used as hardener the resulting mixture should then preferably be hardened at approximately 121 to 174°C.

A plasticizer such as dibutyl phthalate or tricresyl phosphate may be contained in either one or both of the mixtures. The quantity of the plasticizer may be from 0 to approximately 25 weight parts per 100 weight parts of the binder. Preferably, the plasticizer may be in the range from 0 to 10% relative to 100 weight parts of the binder. Typically the amount of plasticizer in the binder is 0. The plasticizer is not particularly advantageous since it tends to boil out of the resulting product and thereby the product could burn.

The binder used in the heat-insulating material has certain important advantages. If heated to several thousand degrees it builds a char structure on the overheated surface and transitions leading from the surface to the char inside. This is characterized by the buildup of carbon-like structures from hydrocarbons and due to the buildup of carbon with a graphite structure and pyrolytic properties. A pyrolytic structure is particularly desirable since it provides a /8 lateral heat transfer through the structure so that the heat transfer through the material on the surface opposite the heat source may be kept at a minimum. The pyrolytic is characterized by the pyrolysis of hydrocarbons by lack of oxygen resulting in formation of carbon-carbon chains.

The carbon formed from the invented binder is a form of hard, cellular-like material formed through pyrolysis. It is a desired component in the heat insulating material for a number of different reasons. One reason is that char is porous, creating a cooling effect through breathing where the gases strike the material and escape. Cooling through breathing is particularly desirable because gases, once striking the structure, will absorb heat from it. The char, however, is not overly porous because if this were so the gases would tend to move through in an explosive fashion, damaging and weakening it thereby. Another reason is that the char layer builds up a black body and is thereby in a position to reflect and irradiate substantial amounts of heat hitting the char surface. Other advantages of the carbon layer are that it is hard and not easy to crack. /9 If the char layer were to crack its heat insulating properties would be lost.

The carbon buildup occurs first through pyrolysis of the epoxy benzine rings. The pyrolysis of the polysulfide builds simple compounds which tend to break up and volatilize. This is the reason why it is desirable to have a substantial amount of epoxies in the binder. It is, however, not desired to diminish the polysulfide too much since the polysulfide controls the elasticity of the heat insulating material.

When the filling materials are heated up they create a series of chemical reactions where each being endothermic, absorb heat from it, and where each at relatively small increase in temperature react with the foregoing. If, for instance, the anhydrous sodium borate and monobasic ammonium phosphate are used as filling materials, the monobasic ammonium phosphate will decompose after a series of succeeding steps into metaphosphoric acid (HPO_3), ammonia and water. The water then will cause the transformation of the anhydrous sodium borate into the hydrate form of the sodium borate. This hydrate form will then progressively decompose in succeeding chemical steps into boron oxide, sodium hydroxide and water. The chemical reactions are reversible since the water created from the composition of the monobasic ammonium phosphate reacts to transform the anhydrous sodium borate into the hydrate form of sodium borate.

The chemical decomposition of monobasic ammonium phosphate begins at approximately 100°C. It occurs at the location where the binder is being modified to char. The chemical reaction occurs as follows:



The gaseous ammonia escapes through the carbon structure buildup from the binder. The decomposition of the monobasic ammonium phosphate, as shown in formula (1) yields approximately 59 kcal heat per absorbing molecule since the decomposition is endothermic. Moreover, the ammonia absorbs heat from the char as it escapes through it.

The phosphoric acid created according to formula (1) decomposes at approximately 225°C in accordance with the following equation:



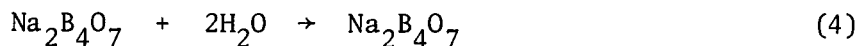
This reaction is also endothermic and yields approximately 16.6 kcal heat per absorbing molecule. The water resulting from this reaction will be absorbed by the anhydrous sodium borate and formation of the hydrate form of the sodium borate will result.

The metaphosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) resulting in accordance with equation (2) decomposes further at approximately 290°C and forms metaphosphoric acid and water in accordance with the following formula:

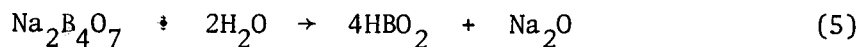


This decomposition is also endothermic and yields approximately 23.8 kcal /11 heat per absorbing molecule. The metaphosphoric acid is a glass-like compound which sublimates past 900°C. The metaphosphoric acid, however, does not sublime before all the reactions described before and below have taken place since all of these essentially have taken place below 900°C. Before it does sublime, however, the metaphosphoric acid functions as a binder in the invented heat-insulating material. The sublimation is endothermic so that additional heat is thereby absorbed.

The water molecules created according to equation (1), as well as those created in accordance with equation (3), combine chemically with the anhydrous sodium tetraborate as follows:



This reaction is particularly desirable because the anhydrous sodium borate melts at approximately 741°C and does not decompose below the temperature of 741°C. The hydrate form of the sodium borate, however, decomposes at approximately 100°C in accordance with the following formula:



This decomposition is endothermic with a heat absorption of approximately 99.4 kcal per molecule.

The chemical compound HBO_2 decomposes further at approximately 167°C in accordance with the following reaction:

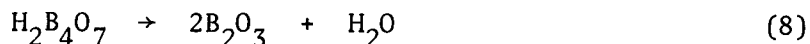


This decomposition is also endothermic. The sodium oxide resulting in accordance with equation (5) and the water molecules created in accordance with equation (6) then combine and build sodium hydroxide in accordance with the following reaction:



Sodium hydroxide melts at approximately 318°C and boils at approximately 1390°C. When sodium hydroxide melts and boils it absorbs heat. The boiling of the sodium hydroxide can be recognized by the yellow flame on the surface of the carbonaceous char.

The boric acid decomposes again and forms boron oxide in accordance with the following reaction:



This decomposition takes place at approximately 276°C and is endothermic. Boron oxide is a glass which is compatible with the carbon structure and has a melting point of approximately 575°C and a boiling point of approximately 1500°C. Testing at a flame temperature of 982°C a small amount of molten glass was found on the surface of carbon. On the other hand, there was a reasonably large amount of glass present when the material was proved at 1650°C, yet the molten glass was essentially preserved by the carbonaceous char. In the flame of the oxygen-acetylene burner at approximately 2465°C a small amount of boron oxide melted and became free-flowing although a substantial proportion vaporized.

Water resulting from the chemical reaction according to equation (8) combines then with the anhydrous sodium borate and from the hydrate form of the sodium borate. This simplifies the decomposition of sodium borate as described above until the sodium tetraborate becomes a decahydrate according to the formula: $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. After the amount required for the catalytic decomposition has been supplied the water excess is absorbed by formation of sodium hydroxide. The above described reaction flow offers several advantages. One of these is that one of the filling materials, namely the decahydrous sodium

tetraborate is more stable than all composition products with exclusion of the metaphosphoric acid formed at the end by the decomposition of the monobasic ammonium phosphate. Another advantage is that a number of chemical reactions take place between approximately 100°C (equation (1) and (5)) and 290°C (equation (3)). The major temperature increase takes place between 100 and 167°C (equation (5) and (6)) and the smallest temperature increase takes place between 100° and 167°C (equation (5) and (6)) and the smallest temperature increase takes place between 276° and 290°C (equations (3) and (8)). With the course of the reaction and of the chemical decompositions resulting in progressively, relatively smaller temperature increases the heat is transferred through the material from the surface exposed to the heat source to the opposite surface and can thereby be held to a minimum. This can also be verified through Figures 2a and 2b. In Figure 2a the surface of the material exposed to the heat is identified with number 20, the opposite surface with number 22. The temperatures between the surfaces 20 and 22 have been schematically shown as 24 when multiple temperature increases of relatively small values take place.

While the heat differential between adjoining positions is relatively small there is a relatively small heat transfer between the surfaces 20 and 22. In contrast to this the temperature increases on 26 are shown schematically and, in fact, in cases where the increases are relatively large. Since the temperature increases are rather irregular there is a large heat transfer in the areas between two succeeding temperature increases. Such high heat transfers are found in conventional materials. The char buildup from the binder simplifies the chemical decomposition of the filling material in the succeeding stages.

The reason for this is that char is porous so that gases built up in the above mentioned reactions flow through the carbon layer in the direction of the material surface exposed to the heat. In particular the movement of water molecules through the carbon simplifies the transfer of the anhydrous sodium tetraborate into the hydrate form of sodium tetraborate on a regenerative basis. Moreover, the porous structure of the carbon simplifies the cooling through venting since the gases absorb heat when they flow through the carbon layer. When the gases which permeate through the carbon reach the surface proper they build a reflecting surface upon the surface of the heat-insulating material

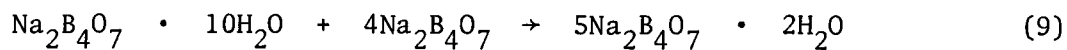
exposed to the heat source. The reflecting surface buildup of the gases diminishes the permeation of the heat into the heat insulating material. Moreover, the gases absorb additional heat after they have built the reflecting surface on the heat insulating surface facing the heat source.

Most of the products resulting from the aforescribed chemical reactions and decomposition are not flammable. Moreover, the use of water on a regenerative basis towards the building of the hydrate of tetraborate and towards the transformation of sodium oxide into sodium hydroxide tends to eliminate unfavorable reactions between water and carbon. Otherwise carbon and water vapor at the high temperatures of the red glowing surface of the material would react instantaneously. These reactions would tend to destroy the material surface in such a manner that the material would be substantially weakened. Moreover, they would foster wide-ranging additional chemical reactions between carbon and water vapor on a progressive basis. Moreover, the carbon layer would be releasing single carbon molecules and weakening itself thereby. /15

The carbon structure is further strengthened through the fire resisting compounds of the glassy metaphosphoric acid (HPO_3) and of the glass-like boron oxide, which represents the end product of the aforescribed chemical reactions. These fire resistant compounds solidify, whereby they hold together and strengthen the carbon structure.

The decomposition and sublimation products were created to build up a reducing atmosphere inside and around the char structure. This can be partially demonstrated in that the char structure is not used up until the base material has been completely covered and stops generating gas and vaporization products.

Other materials may be used in addition to the abovementioned products. Instead of the anhydrous sodium borate Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) may be used as a filling material. The amount of Borax may be set at between 17 and 260 weight parts relative to 100 weight parts of the binder. Preferably, the amount of Borax should be between 35 and 80% relative to 100 parts of the binder. Typically the Borax represents 55 weight parts per 100 parts of the binder. When Borax is used the following relation takes place: /16



The hydrate form of the sodium tetraborate decomposes further in accordance with equations (5) through (8). Borax is not as advantageous as anhydrous sodium tetrachlorate since the 10 Mol water per Mol of the tetrachlorate tend to decompose with a higher velocity in presence of carbon building thereby forming carbon monoxide and carbon dioxide. The formation of carbon monoxide and carbon dioxide result in a reduction of carbon atoms and a consequential weakening of the char layer.

Other materials may also be used as filling material in accordance with this patent. For instance, ammonium biborate ($\text{NH}_4\text{HB}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$), disodium phosphate (Na_2HPO_4), as well as sodium and calcium biphosphate may be used. The phosphates may be favorably used in the preceding equation (1) instead of the ammonium phosphate so that this product is contained in the reaction chain with the tetraborate whereby each reaction will then take place at a relatively /17 smaller temperature increase. The biborate can also be used instead of the borate mentioned in equation (1). Other products may be used, for instance, other borates instead of the abovementioned tetraborates. Moreover, other metals such as potassium, lithium, rubidium, cesium, barium, strontium, magnesium and calcium may be used instead of sodium in the tetraborate.

When ammonium diborate is used the amount implied may be from 17 to 100 weight parts per 100 parts of the binder. Preferably, the amount of ammonium diborate should be from 35 to 80 weight parts per 100 weight parts of the binder. Typically, the amount of ammonium diborate represents 55 weight parts per 100 weight parts of the binder. In addition to the abovementioned, other materials may be used as filling materials. For instance, titanium dioxide, calcium hydroxide, aluminum hydroxide and zirconium dioxide may be contained in the filling material. These filling materials may be used along or in conjunction with others. The hydroxides lose their water molecules upon heating, thus building the metal oxides. The water molecules join then with the anhydrous form of the tetraborate and simplify the chemical decomposition of the tetraborate.

The metal oxides are mostly chemically inert so that they do not decompose to absorb heat; however, the oxide and hydroxides make a contribution to the reflection and reemission of heat radiation from the surface of the heat insulating material. The metal oxides and dioxides provide a relatively high protection of the heat-insulating material to temperatures of approximately 2760°C as /18 opposed to a temperature of approximately 1650°C. Moreover, other filling materials, as illustrated in the following table, may be used at the levels expressed per 100 weight parts of the binder:

Material	Weight Parts	/19
Calcium phosphate, $\text{CaH}_4(\text{PO}_4)_2$	86	
Ammonium phosphate, dibasic	15-87	
Sodium phosphate, monobasic	34.4-85	
Sodium phosphate, dibasic	85	
Sodium phosphate, tribasic	85	
Sodium phosphate, pyrophosphate	85	
Sodium oxalate	85	
Calcium oxalate	37	
Ammonium bromide	4-10.2	
Ammonium sulfate	10-85	
Potassium carbonate	85	
Sodium carbonate	85	
Calcium sulfate	85	
Ammonium hydroxide	40-85	
Calcium hydroxide	38.7-85	
Zirconium hydroxide	85	
Titanium dioxide	34-52.5	
Magnesium oxide	17	
Aluminum oxide	42.7-57.7	
Potassium chloride	85	
Potassium bromide	1-4	
Aluminum fluoride	50.6	
Graphite	34	

Material	Weight Parts
Eccospheres R. silica microballoons	17-24
Burned clay (SiO_2), Cab-O-Sil M5	11

In addition to the above described advantages the heat-insulating material possesses additional advantages. An advantage is that the material may be applied to the part to be insulated in any desired thickness in liquid or plastic or solid form. The heat-insulating material may be applied on any useful surface to provide an effective insulation between the surface and the heat source. The material is in a position to preserve its heat-insulating properties and its structural integrity at ambient temperatures between 18.3 and 85°C over a long period of time even if it has been continuously exposed over a long period of time to the temperatures nearing both extremes of the range. The material is resistant to water, oil, benzene and solvents such as toluene. The material, however, shows a slight swelling after it has been immersed for three days in toluene and reveals strong swelling if it has been immersed for three days in acetone. /20

The material preserves its insulating properties when it is subject to different aerodynamical heating situations and high aerodynamical stress loads. It offers a useful application in the insulation of containers that are subject to high temperatures and high pressures, the insulation of venturi notches and tubes, which carry gases flowing at extremely high speeds and high pressures, the insulation of structures subject to radiation heat and to the high temperatures of combustion products.

Other binders in addition to the mixtures of epoxies and polysulfides have been used with some success; however, these binders have not matched the success of the polysulfide-epoxy-combination. These binders comprise polyurethane, polybutadene, polysulfide (alone), epoxies (alone), furan resins, polyester resins, phenolic resins, silicon resins, 2-pyrol and linseed oil. If furan resin is used as a binder it should be in the range from 10 to 90 weight parts of the resin with epoxy in the range from 90 to 10% of the epoxy resin. Some of /21

these, such as polyurethane do not carbonize, but tend to melt. Consequently, these materials are not fully advantageous. Rubber polymers, such as polybutadiene may be used as well as may also polymers, such as neoprene or butyl rubber or natural rubber. When these materials are used as binders the hardening temperature must be increased.

Epoxies, such as liquid epoxy resins may also be used as binders. In this situation a polyfunctional amine may be used as a hardener or the same result can be had with a polyamide in the stoichiometric range of 50 to 200% or a combination of polyfunctional amines and polyamides in the range of one part to 10 parts of hardener to 9 parts to one part of the other hardener around a joint stoichiometric range of 50 to 200%.

Crease binders composed of approximately 100 weight parts of sodium silicate, 50 parts of calcium sulfate (plaster of Paris), 75 to 125 weight parts of "Fixall" spackling plaster, 100 weight parts of asbestos, 100 weight parts of interior plaster or 100 weight parts of plastic cement may be also employed. With the above binders the filling materials in the following table may be used /22 in the approximate ranges relative to 100 weight parts of the binder:

Material	Range
Borax	50-100
Anhydrous sodium borate	54
Monobasic ammonium phosphate	48
Monobasic calcium phosphate	50-100
Aluminum hydroxide	50
Aluminum oxide	100

If furan resin, polyester resin, phenolic resin, silicon resin and 2-pyrol are used as binders then the following filling materials may be used in the ranges specified and based upon 100 weight parts of the binder:

Material	Range
Oxalic acid	100-175
Borax	55-60
Anhydrous sodium borate	54
Monobasic ammonium phosphate	40-48
Boric acid	40-120
Fumaric acid	67-150
Dibasic ammonium phosphate	45-55
Paraformaldehyde	75-100
Ammonium fluosilicate	150
Eccospheres R	50

The carbonaceous char may be impregnated with molten or solid glass formations such as boron oxide, or with glassy compounds such as metaphosphoric acid, or with highly viscous materials such as sodium oxide or sodium hydroxide, or with a combination of such compounds, as it may give the most appropriate carbon structure for a particular high temperature insulation. These materials, as described before, are mixed with the filling material.

Numerous heat tests were made with the claimed material. For instance, a sample of the preferred material of approximately 0.23 centimeters thickness was applied on a steel plate (4130 steel) of 15 x 15 centimeters and approximately 0.12 centimeter thickness. The weight of this heat insulating sample was approximately 29.34 kg/m². An air-acetylene burner was directed at the material for a continuous period of approximately 50 hours. During these 50 hours the maximum temperature on the back side of the steel plate reached approximately 149°C. The heat flow from this torch was approximately 1,000,800 kcal/kg during the 50 hours of the exposure period. Even though 90% of this heat was reflected by the black body built by the barrier and by the gaseous barrier formed on the surface 55,600 kcal/kg were still absorbed. Approximately 2% of the heat applied was absorbed in the chemical decomposition and sublimation of the several chemical reactions. This proves that the heat gradient carrying the smallest temperature differential reduces the heat quantity transferred through the heat insulating material.

In all of these experiments the temperature of the back side of the material was measured at progressive intervals during the time to which the front side was subject to the heat source. In Figures 3 and 4 the flame of the air-acetylene burner was directed upon the material delivering a temperature of 1650°C and in Figure 5 the flame of the oxygen-acetylene burner directed upon the material generated a temperature of approximately 2760°C.

The invented material, as used according to Figure 3 had the following composition:

Material	Weight Parts
Polysulfide	55.0
Hardener	4.5
Ammonium biborate	47.0
Epoxy	45.0
Sodium phosphate	34.4

The prepared test material of Figure 3 had a thickness of approximately 1.27 cm. Page 3 of 11

The invented material according to Figure 4 had a thickness of 0.7 cm. Novel Page 11 of 11
The material had the following composition:

Material	Weight Parts
Polysulfide	55.0
Anhydrous sodium borate	36.0
Monobasic ammonium phosphate	32.0
Hardener	4.5
Epoxy	45.0

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The material used according to Figure 5 had a thickness of approximately 1.6 cm and the following composition: 25

Material	Weight Parts
Polysulfide	57.5
Hardener	4.25
Anhydrous sodium borate	18.0
Monobasic ammonium phosphate	16.0
Aluminum oxide	40.0
Epoxy	17.7

Figure 6 shows the relationship of the invented material subject to a flame of a temperature of approximately 1650°C which was used for a continued period of 50 hours. The material used in this test had the following composition:

Material	Weight Parts
Polysulfide	55.0
Anhydrous sodium phosphate	36.0
Monobasic ammonium phosphate	32.0
Hardener	4.5
Epoxy	45.0

The coating built from the above material had a thickness of approximately 2.2 cm. It was bound with a steel plate of a thickness of 0.12 cm. As Figure 6 reveals the temperature on the back side of the steel plate was only approximately 149°C while the front side of the steel plate was being continuously subject for a period of 50 hours to a temperature of approximately 1650°C.

Patent Claims

/26

1. A heat insulating material suitable to withstand temperatures of several thousand degrees over a long period of time without complete destruction of the heat insulating properties and characterized by containing a binder which is carbonizable under heat influence and a mixed filling material which chain reacts in such a way that each endothermic chemical reaction produces the previous chemical product, whereby each successive step of the endothermic chain reaction realizes at a higher temperature higher than the temperature created by the previous endothermic reactions.

2. A heat insulating material in conformity with claim 1, characterized in that it contains filling materials able of generating certain gases in the chain reaction in such fashion that they permeate through the carbon layer to the surface of the material, and that through an inter-reaction with the carbon are able to create a heat reflecting surface, and that such filling materials are able to create such chemical products in the chain reaction which decompose endothermically.

3. A heat insulating material in accordance with claim 1, characterized in containing a binder that builds a pyrolytic carbon structure under heat

influence that is representative of a black body, able to reflect heat directed at its surface, whereby such carbon layer is both porous and permeable, and that the filling materials resulting from two compounds which under normal temperature conditions would not react with each other but which, however, are able to react under increasing high temperature under formation of multiple chemical products, from which the chemical products of each preceding endothermic chemical reaction results, whereby, each endothermic chemical reaction in the chain realizes at a higher temperature than the temperature of the chain reaction stage preceding the endothermic chemical reaction. /27

4. The heat insulating material in accordance with claim 3 characterized in containing filling materials upon which the succeeding reactions produce gases capable of permeating through the porous carbon layer and in building a heat reflecting layer upon the surface and additional solid materials which tend to sublimate to the surface of the carbon layer at high temperature and induce additional heat absorption.

5. A heat insulating material in accordance with claim 1, characterized in containing a binder made up of a mixture of a polysulfide and epoxy and a filler composed of a mixture of anhydrous sodium tetraborate and monobasic ammonium phosphate.

6. A heat insulating material in accordance with claim 5, characterized in that the binder contains polysulfide and epoxy in proportions of 1 to 4 weight parts of epoxy to 4 to 1 weight parts of polysulfide.

7. A heat insulating material in accordance with claim 6, characterized thereby that the binder contains as hardener a polyamine in levels of approximately 8 to 12 weight percentage relative to the epoxy weight.

8. A heat insulating material in accordance with claim 1, characterized in that it contains a binder which forms a oxidation resistant carbon layer under heat influence, which is a poor heat conductor and which forms on the surface a porous, pyrolytic black body, able to reflect heat from its surface and which is permeable to gases, whereby the binder contains benzene rings to simplify the carbonization, and that it contains at least 2 filling materials mixed with it, able of react in succeeding stages endothermically /28

under generation of gases, which defuse through the porous carbon body to the surface of the carbon layer and induce the heat reflection from its surface, whereby the filling materials generate successively additional chemical products, from which chemical chain reaction each succeeding chemical products result and whereby each filling material reacts at progressively higher temperature, whereby each temperature increase becomes proportionately smaller and which generates as an end product solid materials which sublime at higher temperatures.

9. A heat insulating material in accordance with claim 8, characterized by having filling materials consisting of a mixture of one phosphate and one borate.

10. A heat insulating material in accordance with claim 8, characterized in having a binder consisting of a mixture of one polysulfide and one epoxy.

11. A heat insulating material in accordance with claim 8, characterized by having a filling material in an anhydrous condition which only reacts at high temperature and whereby as a consequence of the chemical reactions water molecules are so created which react with the anhydrous filling material under formation of the hydrate form of such filler, whereby the hydrate form of the filler then decomposes chemically at a lower temperature.

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12. A heat insulating material in accordance with claim 1 which is solvent stable and which preserves its properties under normal ambient temperatures and characterized in that the first and second fillers contain oxygen and hydrogen able to create water molecules upon heating, whereby these fillers under normal ambient temperatures are chemically inert even if mixed with each other, and whereby the fillers of each stage are able to react chemically and endothermically at progressively higher temperatures, departing from a particularly high temperature, whereby each temperature increase is proportionately small and which builds such chemical reactions under generation of gases, whereby at least one of the end products of the chemical reactions under higher temperatures above the temperature of the preceding chemical reaction will tend to sublime endothermically, and whereby one of the fillers shall be relatively stable and able to react regeneratively with the water molecules created by its own chemical

reaction and from other materials and is able to build relatively unstable hydrates of the same binders, which simplify the chemical reaction of these fillers in the succeeding stages, and that the binder is able to build a porous carbon layer at higher temperatures, and whereby the gases contained in the filling materials tend to create a diffusion cooling effect through their passage in the layer, whereby the char represents the pyrolythic black body able to reflect heat from its surface.

13. A heat insulating material in accordance with claim 12 characterized in that the first filler contains phosphates and the second filler borates.

14. A heat insulating material in accordance with claim 12 characterized in that the binder consists of a mixture of one polysulfide and one epoxy. /30

15. Process for the manufacture of a heat insulating material in accordance with claims 1 through 14 characterized thereby in that an epoxy and filler are mixed to create the first mixture, and whereby the filling materials consists of two different substances, which do not react with each other at normal ambient temperatures, but which, however, are able to chain react at increasing higher temperatures above the usual ambient temperatures under formation of multiple chemical products where each endothermic chemical reaction results in the previous chemical product, whereby each successive endothermic chemical reaction in the chain takes place at a higher temperature than the proportional temperature of the preceding endothermic chemical reaction of the chain, where the one polysulfide and the fillers and a hardener for the epoxy are added to a second mixture, and where in conclusion the first and the second mixture are mixed to produce the heat insulating material.

16. A process in accordance with claim 15 characterized in that the epoxy is introduced in quantities of 4 to 1 weight parts of epoxy to each 1 to 4 weight parts of polysulfide.

17. A process in accordance with claim 15 characterized in that a polyamine in a range of 8 to 12 weight percentage parts relative to the epoxy weight is used as hardener.

18. A process in accordance with claim 16 characterized in that phosphates and borates are used as fillers.

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19. A process in accordance with claim 1, characterized in that as first /31
and second filling materials substances are used containing oxygen and hydrogen
which are able to build water molecules under heating, whereby these filling
materials even if mixed together will not chemically react at normal ambient
temperatures and which are able to react chemically in a chain reaction at pro-
gressively higher temperatures above a given high temperature which may be pro-
portionately small and which build chemical products including water and are
able to undergo further chemical reactions under formation of gases, whereby at
least one of the end products of the chemical reactions at a higher temperature
than the temperature of the preceding chemical reaction are able to sublime
endothermically, whereby one of the filling materials is relatively stable and
able to regenerate itself chemically with the water molecules built up from its
own chemical reaction and from other materials under formation of a relatively
unstable hydrate of this same filling material, and which helps promote the
chemical reaction of this filling material in the chain reaction, then a polysul-
fide and a hardener for the epoxy are mixed to create the second mixture by ad-
dition of the first and second filling material and whereby then at room temper-
ature the first and second mixtures are added to one another under formation of
the heat insulating material.

20. A process in accordance with claim 19 characterized in that an anhy-
drous borate is used as the first filling material and a basic phosphate as the
second filling material.

21. A process in accordance with claim 19 characterized by using the epoxy
in quantities of 1 to 4 weight parts of epoxy to 4 to 1 weight parts of polysul-
fide and where a polyamine in quantities of 8 to 12 weight percent relative to
the epoxy weight are used as a hardener.

22. Process in accordance with claim 19 characterized in that epoxy and /32
polysulfide are used in approximately the same weight proportions.

23. A heat insulating material in accordance with claim 1 able to with-
stand high temperatures for long periods of time without total self-destruction
and characterized in that the first and the second filling material contain oxy-
gen and hydrogen, so that under heating they are able to produce water molecules,
that the first and the second filling material under normal ambient temperatures

even if mixed with one another shall not react chemically and which, however, are able to react endothermically with each other in a chain reaction at progressively higher temperatures than a relatively high temperature whereby each temperature increase is relatively small and which yields chemical products which shall include water, and which are able to enter additional chemical reactions and form gases whereby at least one of the end products of a chemical reaction at increased temperatures above the temperature of the preceding chemical reaction is able to sublime endothermically, and whereby one of the filling materials shall be relatively stable and able to regenerate chemically with the water molecules built from its own chemical reaction and of other materials under formation of a relatively unstable hydrate of this filling material which will tend to promote the succeeding step of the chemical reaction of the filling material.

24. A heat insulating material in accordance with claim 23 characterized in that a metal oxide is contained in the filling material.

25. A heat insulating material in accordance with claim 23 characterized in that it contains a binder for the filling material. /33

For: Universal Propulsion Co.
Riverside, California, U.S.A.

(Dr. H. J. Wolff)
(Attorney at Law)